

S Scarrah, Warren P
662.669 Conversion of
N7cgo safflower oil to
1999 diesel via the
soap-pyrolysis
process

RENEWABLE ENERGY REPORT LIBRARY

CONVERSION OF SAFFLOWER OIL TO DIESEL VIA THE SOAP-PYROLYSIS PROCESS

STATE DOCUMENTS COLLECTION

FEB 27 1990

MONTANA STATE LIBRARY
1515 E. 6th AVE.
HELENA, MONTANA 59620

PLEASE RETURN

Prepared for

MONTANA DEPARTMENT of NATURAL RESOURCES and CONSERVATION

MONTANA STATE LIBRARY
S 662.669 N7ca9 1989 c.1 Scarrish
Conversion of safflower oil to diesel vi



3 0864 00064457 8

DATE DUE

MAY 3 2001
APR 28 2004

CONVERSION OF SAFFLOWER OIL TO DIESEL
VIA THE SOAP-PYROLYSIS PROCESS

by

Dr. Warren P. Scarrah
Department of Chemical Engineering
Montana State University
Bozeman, Montana 59717
Phone: (406) 994-5926

Prepared for
Montana Department of Natural Resources and Conservation
Grant Agreement RAE-86-1065

Total Project Cost: \$75,166
DNRC Grant: \$54,166

February 1989

Project Scope

The researcher studied the conversion of safflower oil into diesel fuel satisfactory for both medium- and high-speed diesel engines. Safflower oil is a renewable resource particularly attractive for Montana, because our arid climate is well suited for its growth and it is excluded from federal farm program restrictions. The safflower oil was first converted into soap which was then pyrolyzed to produce diesel fuel. A simple method for making soap was developed and the process variables optimized for both the soap production and pyrolysis processes.

This report was prepared under an agreement funded by the Montana Department of Natural Resources and Conservation. Neither the Department nor any of its employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe on privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Natural Resources and Conservation or any employee thereof. The reviews and opinion of authors expressed herein do not necessarily state or reflect those of the Department or any employee thereof.

ABSTRACT

The purpose of this research was to study the soap-pyrolysis process for making fuel suitable for use in a diesel engine. The process involved converting safflower oil into a soap and then pyrolyzing the soap to obtain the diesel range fuel.

The two fuel properties selected to evaluate the soap-pyrolysis process were (1) the yield of fuel and (2) the thickening properties of the lubrication oil contaminated by a five weight percent mixture of vegetable fuel when subjected to simulated engine crankcase conditions. The change in the initial viscosity of the fuel-lubrication oil mixture compared to the viscosity after 48 hours indicated the thickening properties. Although there were differences at the beginning, the final viscosities of the mixtures were all less than or comparable to the lubrication oil alone. Therefore, fuel yield became the principal criterion for evaluating the effects of process variables.

The experimental program was divided into five milestones. Milestone one was an investigation of these pyrolysis process variables: the age of the soap, the glycerol content of the soap, the fatty acid content of the soap, calcium versus magnesium soaps, and the separation of the fuel by distillation into different fractions; also, any effects due to fuel aging were observed. Milestone two was a study of the addition of calcium hydroxide prior to pyrolysis to promote the formation of hydrocarbons rather than aldehydes or ketones. The third milestone involved a comparison of soap production methods: the precipitation process and the fusion process with water and toluene as solvents and without any solvent. Finding effects of the amount of unsaturation in the fatty acid component of the vegetable oil was the purpose of milestone four. The determination of the values of the process variables to optimize the fuel yield was the objective of the fifth milestone.

It was concluded that, to increase fuel yield (1) the soap should be washed to remove glycerol, (2) calcium rather than magnesium soaps should be used, (3) calcium hydroxide should not be added prior to pyrolysis, (4) the fusion soap-making process without a solvent should be used, (5) it would be better to have higher oleic acid ester and lower linoleic ester contents in the safflower oil, and (6) stoichiometric quantities of calcium hydroxide should be used to make the soap. The optimum fuel yield was found to be about 40 lb. fuel per 100 lb. safflower oil.

TABLE OF CONTENTS

	Page
ABSTRACT.....	ii
LIST OF ILLUSTRATIONS.....	iv
LIST OF TABLES.....	v
INTRODUCTION.....	1
RESEARCH OBJECTIVES.....	4
EXPERIMENTAL DESCRIPTION.....	6
Soap Production.....	6
Pyrolysis.....	6
Polymerization.....	8
Acid Number.....	11
Iodine Value.....	14
Nuclear Magnetic Resonance.....	14
Distillation.....	15
Yield.....	15
RESULTS AND DISCUSSION.....	17
Pyrolysis Studies.....	17
Aged Versus Fresh Soaps.....	17
Glycerol Content of the Soaps.....	19
Fatty Acid Content of Soaps.....	21
Calcium Versus Magnesium Soaps.....	23
Distillation Results.....	24
Storage Effects.....	27
Results for Pure Linoleic Acid.....	27
Pyrolysis With and Without Calcium Hydroxide Reactant	27
Soap Production.....	32
Unsaturation Studies.....	35
Soap-Pyrolysis Process Optimization.....	40
OPTIMIZED PROCESS DESCRIPTION AND PROCESS FLOWSHEET.....	51
CONCLUSIONS AND RECOMMENDATIONS.....	53
TECHNOLOGY TRANSFER ACTIVITIES.....	55
APPENDICES.....	56
Appendix 1. Sample Calculations.....	57
Appendix 2. References Cited.....	60

LIST OF ILLUSTRATIONS

Figure	Page
1. Soap-Making Process Apparatus.....	7
2. Pyrolysis Apparatus With Stainless Steel Vessel.	9
3. Pyrolysis Apparatus With Glass Vessel.....	10
4. Polymerization Apparatus.....	12
5. Viscometer and Temperature Bath.....	13
6. Variable Levels for Sequential Simplex Optimization Technique.....	42
7. Variable Levels for Complex Method of Box Optimization Technique.....	43
8. Variable Levels for the Factorial Experimental Design.....	45
9. Block Flowsheet for the Soap-Pyrolysis Process for Converting Safflower Oil to Diesel Fuel.....	52

LIST OF TABLES

Table	Page
1. Fatty Acid Distribution in Safflower Oil.....	2
2. Typical Ranges for Diesel Fuel Types.....	16
3. Fuels from Aged and Fresh Soaps.....	18
4. Fuels from Soaps With Different Amounts of Glycerol.....	20
5. Fuels from Soaps With Different Free Fatty Acid Contents.....	22
6. The Total Distillate Versus the #2 Range.....	25
7. Viscosity Results for Diesel Fuel Types.....	26
8. Aged Versus Fresh Fuels.....	28
9. Experiments With/Without Calcium Hydroxide Reactant.....	30
10. Viscosity Results of Fuels With/Without Reactant.....	31
11. Results of Fuels from Different Soaps With and Without Solvent.....	34
12. Yields of Fuels from Different Soaps With and Without Solvent.....	36
13. Results of Fuels from Different Acid Soaps.....	38
14. Results for the Complex Method of Box.....	44
15. Results from the 3^2 Factorial.....	46
16. Variable Levels Used for Optimization.....	48
17. Final Run Results.....	49



INTRODUCTION

In the mid-1980s the United States was poised insecurely between an energy crisis it had momentarily averted and an energy future it could not confidently predict. The energy crisis that lasted from 1973 to 1978 was triggered by a sudden but brief Arab embargo upon petroleum exported to the United States, quickly followed by several years of sharply rising world petroleum prices. The United States was forced to recognize it had become heavily dependent upon imported petroleum and could no longer satisfy its own rapidly rising energy demands from its existing domestic energy production. More ominously, it appeared the United States might face a shortage of petroleum within a few decades. Experts remained divided and uncertain about the future [1]. An alternative source of energy to take the place of fossil fuels might someday help alleviate this problem.

Vegetable oils show much promise as replacements or extenders for diesel fuels. Theoretically, a farmer could plant a fraction of his land in oil-producing crops and use the fuel produced to run his entire operation. Seed oils such as safflower oil have received considerable attention as direct substitutes or additives for fuels suitable for use in a diesel engine. Safflower oil has the attraction of being grown easily in Montana. It would be of great interest to the agriculture community to see safflower oil replace diesel fuel, because farmers then wouldn't have to rely on fossil fuels with fluctuating prices and finite availability, and could then be more independent and in charge of their own destiny. Researchers estimate agricultural fuel needs for the United States could be met by planting approximately 10 percent of the total cropland with oilseed crops [2]. As an added benefit, vegetable oil processing yields meal high in protein for animal feed as a by-product [3].

Despite the advantages of using vegetable oil for diesel fuel, there are still economic problems. Collins show that diesel prices would have to double or triple before even the best vegetable oils would become competitive [4]. In general, if a raw material such as diesel fuel becomes scarce, its price will rise. Since the relationship between price and supply is not absolute, the price of diesel fuel could easily change [5].

The difference in chemical structure between diesel fuel and vegetable oils is also responsible for problems: (1) vegetable oils form carbon deposits inside direct injection engines and (2) vegetable oils carried into the crankcase polymerize on contact with the lubrication oil, leading to eventual engine failure [6]. Vegetable oils are esters formed by the combination of glycerol with three fatty acids. These fatty acids are straight-chained, monocarboxylic acids that can be either saturated or unsaturated. Saturated would be without any carbon double bonds, and unsaturation is a measure of the carbon double bonds. The fatty acid distribution of safflower is given in Table 1. It has been found that the carbon deposition problem can be solved either by

Table 1. Fatty Acid Distribution of Safflower Oil [7]

<u>Fatty Acid</u>	<u>Percentage</u>	<u>Composition</u>	<u>No. of Double Bonds</u>
palmitic	6.4	$C_{16}H_{32}O_2$	0
stearic	3.1	$C_{18}H_{36}O_2$	0
arachidic	0.2	$C_{20}H_{40}O_2$	0
oleic	13.4	$C_{18}H_{34}O_2$	1
linoleic	76.6 - 79.0	$C_{18}H_{32}O_2$	2
linolenic	0.04 - 0.13	$C_{18}H_{30}O_2$	3

using indirect injection engines or by transesterification. The net effect of transesterification is to replace one large triglyceride ester with three smaller esters. The principal change in physical characteristics of the transesterified vegetable oil is a significant reduction in viscosity compared to the unmodified vegetable oil. This lowering in viscosity appears to prevent the formation of carbon deposits [8].

Transesterification does not necessarily prevent the previously mentioned polymerization problem. The mechanism of polymerization is thought to occur by oxygen first attacking a carbon double bond with the carboxyl groups acting as a catalyst in the reaction [9]. Therefore, the polymerization problem should be able to be solved by a modification of the chemical structure of vegetable oils. The double bonds could be removed by hydrogenation, but this results in a fuel that is a solid at room temperature. Decarboxylation or removal of the carboxyl groups could be accomplished by thermal means with or without the aid of catalysts.

A project that started with work by Hiebert dealt primarily with decarboxylation, and this investigation used his results and continued work in this area [8]. Hiebert found that by converting the safflower oil to a soap and then pyrolyzing the soap to obtain a liquid diesel-range fuel worked the best of the techniques he tried. The chemical structure of the safflower oil was modified in that it was first converted into two products -- soaps (the salts of fatty acids) and glycerol that were subsequently separated. The pyrolysis (decarboxylation) of the soaps mostly removed oxygen to leave aldehydes, ketones, and hydrocarbons. The resulting fuel had relatively low acid numbers (a measure of the free fatty acid content) and significant unsaturation (a measure of the carbon double bonds). This procedure significantly reduced thickening effects measured by kinematic viscosity. A 375 percent increase in kinematic viscosity in 64 hours is considered a failure in lubrication oil tests [10]. This current project was an attempt to improve and learn more about the soap-pyrolysis process for making fuel from safflower oil that could be used in a diesel engine.

RESEARCH OBJECTIVES

The experiments performed for this soap-pyrolysis research have been divided into five milestones. The purpose of the first milestone was to investigate the effects of a number of pyrolysis process variables that might have been important to fuel yield and quality. Soap production was not addressed in this milestone; in fact, rather than starting with safflower oil, linoleic acid (its principal component at 76.6 to 79.0 percent) was used to make the soap [10]. By using a simpler, representative soap, the effects of the processing variables were expected to be more apparent and not confused by the presence of soaps from a number of different fatty acids. High speed lubrication oil was used for the polymerization tests. The high speed lubrication oil is a 30-weight oil.

Six specific process variables were investigated for this first milestone. First, soaps that had been aged were compared with fresh soaps to see how this affected the fuel. Second, because the soap making could be simplified if the glycerol did not have to be removed prior to pyrolysis, comparisons were made between soap without glycerol, soap with an amount of glycerol added equivalent to that produced in the soap making, and soap with an intermediate amount of glycerol consistent with its partial removal. Third, the fatty acid content of the soaps was varied to see how this variable affected the fuel. Fourth, calcium and magnesium soaps were compared because literature indicates these soaps have similar properties. However, the magnesium soaps would probably have lower pyrolysis temperatures, which could change the nature of the fuel [11]. Fifth, a typical diesel fuel fraction of the distillate was compared to the total distillate for differences in polymerization characteristics. Also, different fractions of the distillate were compared with one another. Sixth, any changes in the fuel due to storage might have had an effect on its polymerization properties. Oxidation from contact with air could have caused polymerization. Tests were made on fuels when they were fresh and after they had been stored for a period of time.

The experiments completed for the second milestone compared pyrolysis with and without the use of calcium hydroxide (Ca(OH)_2) reactant. Linoleic acid was again used rather than safflower oil to prepare the soaps so as not to confuse the processing variables by the presence of soap from a number of different fatty acids. Another purpose of this milestone was to compare fuels made from pyrolysis with and without the use of calcium hydroxide reactant with both medium and high speed lubrication oils. High speed lubrication oil is a 30-weight oil, and medium speed lubrication oil is a 40-weight oil. The addition of calcium hydroxide was made to the soap just prior to pyrolysis.

The experiments for the third task concentrated on the soap production process. Safflower oil was used to prepare the soaps for this milestone, because it was important to compare the fuel yields obtained from the vegetable oils using different soap

production methods. A multi-step precipitation process was compared to the single-step fusion method for the production of the soaps. In addition, non-aqueous solvents with varying concentrations were investigated with the fusion method, along with not using a solvent for the process.

The fourth milestone was an attempt to investigate the importance of the degree of vegetable oil unsaturation. Exploratory research in this lab has indicated that converting the safflower oil to a soap prior to pyrolysis significantly decreases the role of unsaturation in the polymerization of lube oils, but more information was necessary [8]. The approach used for this milestone involved converting fatty acids with various degrees of unsaturation or number of carbon double bonds to soaps and then comparing the pyrolysis products for any differences that might be found. High speed lubricating oil was used for the polymerization tests. The fatty acids used in this milestone were different only in the number of carbon double bonds.

The last milestone was to optimize the soap-pyrolysis process for making fuel suitable for use in a diesel engine. The results from the first four milestones helped identify important process variables and techniques that were to be optimized. It was now the purpose to put all this information together and determine the most desirable techniques and levels of variables for the soap-pyrolysis process for making diesel fuel from safflower oil.

EXPERIMENTAL DESCRIPTION

Soap Production

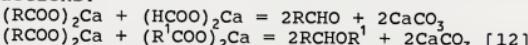
Two methods were used to prepare the soaps for these experiments. The fusion method was employed for most of these runs. The process consisted of the following steps. First, 200 grams of acid (oleic, linoleic, or linolenic) or safflower oil was heated to 100° C. Second, a solution consisting of the alkali hydroxide (calcium hydroxide or magnesium hydroxide) with or without a solvent (demineralized water or toluene) was vigorously stirred in. Magnesium hydroxide was used only to prepare the magnesium soaps in the pyrolysis studies. Toluene was used only as a solvent in some of the soap production experiments. Next, the soaps were allowed to cool, which took several minutes. After the soaps had dried, they were ground into uniform chunks using a hand grinder.

The precipitation method was also used to prepare the soaps. First, 200 grams (in some cases 180) of linoleic acid was heated to 100° C. Second, a solution consisting of sodium hydroxide and demineralized water was vigorously stirred in. This process formed a solid sodium soap. Third, the sodium soap was separated into two batches for easy handling, each of which was dissolved in 500 ml of water. Each batch was then mixed with a solution of calcium chloride and demineralized water and stirred. This process of ion exchange precipitated out the calcium soap. Finally, the two batches of soap were combined and washed with demineralized water to remove any sodium soap or calcium chloride, since they are both water soluble and the calcium soap is not.

Soap reactions were performed at atmospheric pressure in a 1,000 ml glass batch reactor with a glass top. The 1000 ml reactor and glass top were both purchased from Ace Glass, product Nos. 6506-35 and 6485-16. A thermocouple measured the temperature, and a powerstat was used to control the heat supplied to the reaction vessel by a electric heating mantel. The setup for the soap making process is illustrated in Figure 1.

Pyrolysis

Pyrolysis is the process of heating the soaps and condensing the resulting vapors to obtain the diesel fuel. Literature indicates that pyrolysis of calcium soaps leads to the formation of aldehydes (RCHO) and ketones (RCHOR') shown in the following reactions:



Maximum liquid temperatures were about 815° F; this maximum was chosen to prevent damage to the heating mantel. Pyrolysis reactions were carried out in a 500 ml stainless steel reactor vessel; however, this was replaced by a 500 ml glass reactor after several experiments into the pyrolysis studies. The glass

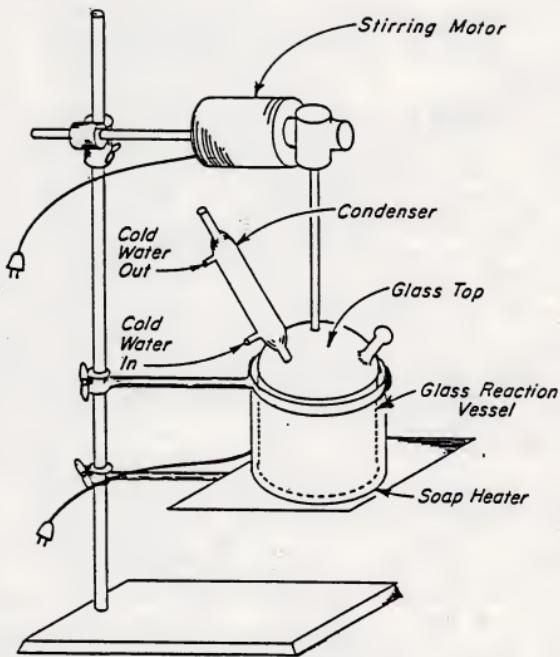


Figure 1. Soap-Making Process Apparatus

reactor was used for the rest of this project. These were both purchased from Ace Glass, product Nos. 6497-05 and 6927-22. The equipment used with both the stainless steel and glass pyrolysis vessels is shown in Figures 2 and Figure 3.

The reason the stainless steel vessel was initially chosen was its ease of cleaning compared to the glass vessel. The change to the glass vessel in this study was implemented because the product yields were significantly lower with the stainless steel vessel than those obtained with the glass vessel during the previous investigation [8]. This change resulted in a significantly greater yield in the current study. The possible reasons for this yield difference are discussed in the "Aged Versus Fresh Soaps" part of the section called "Pyrolysis Studies."

The soap was first put into either the stainless steel or glass reaction vessel with a glass connector between it and the condenser. The condenser then emptied into a separatory funnel. Fiberglass insulation was packed around the top of the pyrolysis apparatus to minimize heat loss. The 500 ml glass reactor was a two-necked flask. The first neck led to the condenser where the vapor temperature was measured, and the second neck was used to insert a thermocouple which measured the liquid temperature. A quarter-inch, glass-covered magnetic stirring bar was inserted in the bottom of the flask to keep the soap well mixed. The 500 ml stainless steel reactor with a glass top was also used for pyrolysis. The glass top had three necks -- the first neck was for the motor-driven stirrer, the second for the thermocouple to measure the liquid temperature, and the third to measure the vapor temperature just before it reached the condenser. Heat was supplied by a different heating mantle than the one used for soap production.

Polymerization

The purpose of polymerization experiments was to simulate crankcase oil conditions in a diesel engine for determining thickening effects due to adding a five weight percent concentration of the fuel. The kinematic viscosity measured in centistokes was used as the measure of thickening effects. The reactions were carried out at 150° C in 100 ml glass batch reactors using 50 ml of lubrication oil. Ten parts per million of a soluble copper form (cupric acetylacetone or CuAcAc) was used as a catalyst, and oxygen was bubbled through at the rate of 3 cc per 15 seconds. The high speed lubrication oil was Amoco Super HD11 SAE 30W, while the medium speed lubrication oil was Unocal SAE 40. These commercial lubrication oils contain lubrication oil additives that affect polymerization. Since effects of vegetable oil fuel on commercial lubrication oil were the focus of this research, no attempt was made to study how additives affect the mechanisms of polymerization. The 100 ml glass reactors were put into a custom-built constant temperature bath. Eight different samples could be tested simultaneously. The

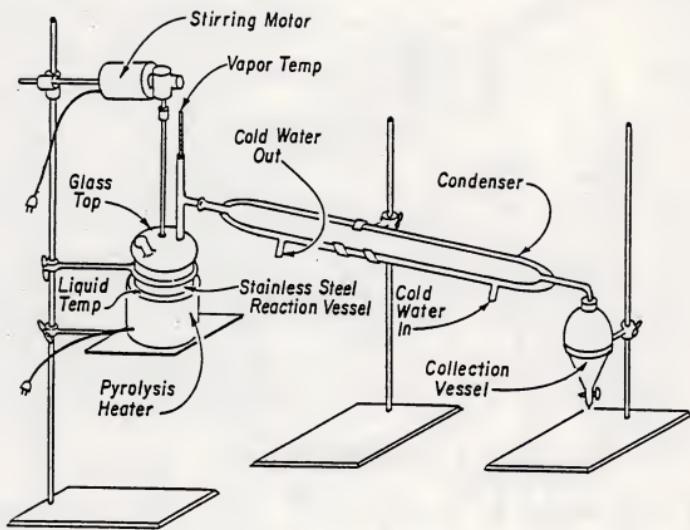


Figure 2. Pyrolysis Apparatus With Stainless Steel Vessel

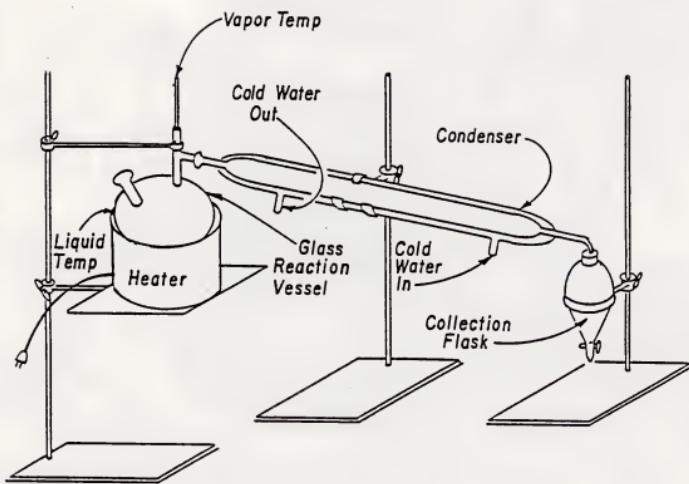


Figure 3. Pyrolysis Apparatus With Glass Vessel

apparatus was arranged so that the bath was under a hood. The polymerization apparatus is shown in Figure 4. Several pieces of equipment were used for the constant temperature bath, and all were from Ace Glass. These were: adapter #11 THD 24/40, product No. 5261-37; test tube, product No. 8752-02; 300 mm pore c tubes, product No. 7202-16; 11 mm nylon bushing, product No. 7506-02; 24/40 bearing c, product No. 8042-115; adapter inner, product No. 5028-30.

Evaporation of vegetable oil fuels in the polymerization apparatus was considered to be a possible problem. Evaporation of the soap-pyrolysis fuels would result in thickening measurements representing only the lubrication oil. Many of the experiments with the high-speed lubrication oil ended up with a kinematic viscosity approximately the same as the control polymerization tests. The control polymerization tests contained the lubrication oil and no added soap-pyrolysis fuel. Because of previous work [8], evaporation was not considered likely. While current work had measurements for kinematic viscosity initially and after 48 hours in the polymerization apparatus, previous work took measurements every 10-12 hours up to 72 hours. The earlier work showed the kinematic viscosity continued to increase above the neat lubrication oil after the 48-hour measurement. Therefore, evaporation of soap-pyrolysis fuels was only a remote possibility. However, future work in this area should be considered.

A viscometer was used to measure the kinematic viscosity at 40° C. A drawing of the viscosity-measuring apparatus is given in Figure 5. The technique used was to add 8 ml of sample to the viscometer and let it stand for 10 minutes. Then the time in seconds was recorded on a stopwatch as the oil traveled between two marks on the viscometer. This was then multiplied by a calibration number to convert it into kinematic viscosity in centistokes. The viscometer was a Canon-Fenske viscometer, No. L799, size 350, report No. 21859. This viscometer was calibrated at 40° C and 100° C. The initial viscosity was measured, and then the sample was put into the 100 ml glass reactors which were placed in the constant temperature bath for 48 hours. At the end of this time the final viscosity reading was taken. Under previous work done on this project [8], it was shown that the thickening properties of the fuel were apparent after 48 hours; the kinematic viscosity using straight safflower oil had increased 110 percent from about 95 to 200 centistokes, while using the safflower soap decomposition product had led to approximately a 22 percent increase from about 90 to 110 centistokes.

Acid Number

The acid number of an oil or oil product is the relative measure of free fatty acid content. The procedure used is described in ASTM D 466-78. This involved dissolving the diesel range product in 95 percent ethanol and heating until boiling.

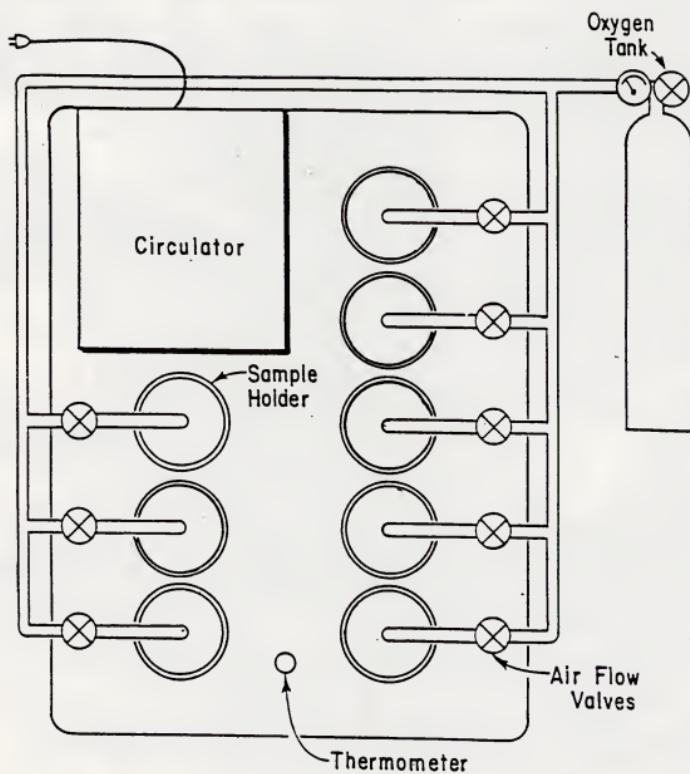


Figure 4. Polymerization Apparatus

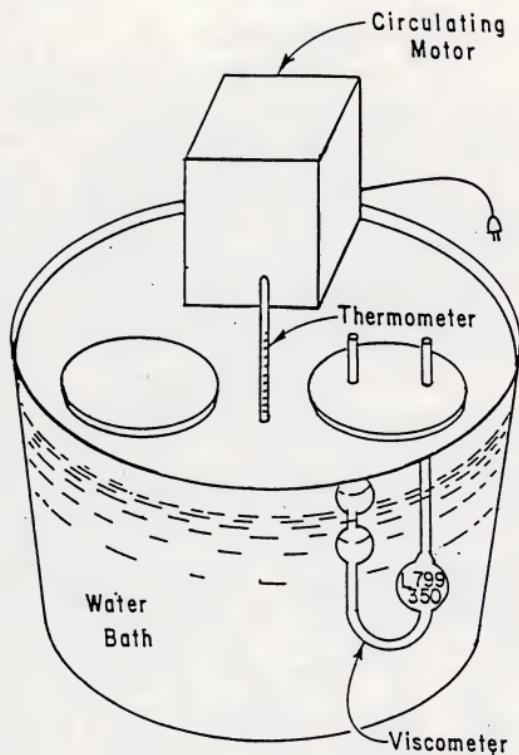


Figure 5. Viscometer and Temperature Bath

Then a titration procedure was used with phenolphthalein as the indicator until the end point was found. The base used for the titration was potassium hydroxide with a normality of close to 0.1.

Iodine Value

The iodine value is the relative measure of unsaturation, i.e., the carbon double bonds, present in the sample. The method used was the Wijs procedure performed according to ASTM D 1959-69. This method has been shown to give accurate results for oils and their derivatives with nonconjugated double bonds. These are the only type present in safflower oil and its derivatives. The procedure was to add 20 ml of carbon tetrachloride and 25 ml of Wijs solution to the diesel sample. This was to be stored in the dark for one hour. After an hour, 20 ml of 15 percent potassium iodide and 100 ml of demineralized water were added. This was then titrated with sodium thiosulfate solution using starch as the indicator. Simultaneously, blanks had to be titrated that were made up of 25 ml of Wijs solution, 20 ml of the 15 percent potassium iodide solution, and 100 ml of demineralized water.

Nuclear Magnetic Resonance

The carbon-13 nuclear magnetic resonance spectrometer (NMR) used was a Bruker WM-250 with an Aspect 2000 computer. The NMR spectra provided qualitative information about the functional groups attached to the carbon molecules. Several parameters had to be tested in order to determine the appropriate settings to use for these oil products. These were receiver gain, receiver delay, and the number of scans. The receiver gain varies with the concentration differences. An appropriate receiver gain would be set so the free induction decay is two centimeters above and below the screen midline. A typical receiver gain for these samples was 1600. The receiver delay is the time between scans. This was already set by choice of the other parameter. A typical receiver delay was around two seconds for these samples. Enough scans should be taken to give a good signal-to-noise ratio that varies by the square root of the number of scans. As the concentration of the sample is increased, a lower number of scans are needed. The 1.5 ml sample of oil was mixed with 0.5 ml of solvent (deutero chloroform). This fairly high concentration required only 500 scans to give good results.

There were several areas of interest in the NMR spectrum. The unsaturation region occurred between 110 to 140 parts per million. The carboxylic acid region was found at 180 parts per million. Esters were found at 170 parts per million. Ketones were from 205 to 208 parts per million. Finally, solvent had three peaks with the middle one at 77 parts per million. All peaks were interpreted relative to the peak provided by the solvent.

Distillation

Distillations were done to determine volatility characteristics of products from the pyrolysis tests. The method used is described in ASTM D 86-78. Tom Davis, a chemical engineer at the Farmers Union Central Exchange in Laurel, Montana, provided the typical ranges for diesel fuel listed in Table 2. It should be noted these ranges vary with the season. The apparatus used included the same 500 ml glass reactor used in pyrolysis, a vapor temperature thermometer, a water-cooled condenser, and a glass recovery flask. The procedure used was to heat the organic product slowly. The vapor would condense and collect in a recovery flask. The product was distilled in order of lightest to heaviest as the temperature was increased. The first and lightest material to come off was a very light yellow. As the temperature was increased, the color of the product went to brown. The heaviest diesel that came off was a dark brown color with a green tint. The differently colored products did not stay separate as they mixed in the recovery flask.

Yield

Yield was calculated two ways. When the various acids were used to make the soap and in the soap production study that used safflower oil to make soap, the yield was computed per 100 grams of dry soap, because the effects of the process variables were of primary importance. This was done by taking the weight of organic product collected and dividing it by the weight of soap charged minus the water product. A second way to calculate yield was used when safflower oil was charged, because it was important to compare the fuel yields from the starting vegetable oils. This yield was calculated per 100 grams of total safflower oil used. This was done by taking the weight of organic product collected and dividing it by the soap charged for pyrolysis. Then this number was multiplied by the total weight of soap and divided by the weight of safflower charged.

Table 2. Typical Ranges for Diesel Fuel Types

<u>Diesel Fuel Type</u>	<u>Initial (°F)</u>	<u>End Point (°F)</u>
heavier-#3	500	720
regular-#2	430	625
lighter-#1	315	520

RESULTS AND DISCUSSION

The results of these soap-pyrolysis experiments will be separated into five sections corresponding to the principal milestones that were performed: pyrolysis studies, pyrolysis with and without calcium hydroxide reactant, soap production, unsaturation studies, and soap-pyrolysis optimization.

Pyrolysis Studies

Aged Versus Fresh Soaps

The first set of experiments compared polymerization properties of fuels prepared from (1) soaps that had been aged for two months prior to pyrolysis and from (2) fresh soaps aged three days before pyrolysis. The soap was prepared by the fusion method using linoleic acid and 50 percent excess calcium hydroxide mixed with 71 grams of demineralized water. High speed lubrication oil was used for the polymerization tests. Table 3 gives the results of these experiments. The fuels obtained from both the aged and fresh soaps did not differ significantly. The acid numbers of the fuels from the aged soaps were both 0.7, while those from the fresh soaps were 1.0 and 1.4. The iodine values of the fuels from the aged soaps were 136 and 141, while those from the fresh soaps were 149 and 150. NMR spectra confirmed the results of small acid numbers and significant unsaturation. The yields of the fuel from the aged and fresh soaps were not comparable because the pyrolysis apparatus had been changed from stainless steel to glass (the effects of this change will be discussed later in this section). Pyrolysis was performed in glass apparatus for the aged soaps and stainless steel apparatus for the fresh soaps. Yields are grams of fuel per 100 grams of dry soap. The pyrolysis vapor temperatures were much lower with the stainless steel than the glass apparatus. When the stainless steel pyrolysis vessel was used, the maximum vapor temperatures were in the range of 200-210° F while they reached 400° F with the glass vessel.

The liquid product formed several layers, and recovery was considered complete when the time between drops of product falling into the separatory increased to about 10 seconds. The lightest and first of the products came out as a clear water layer. The organic layer was next. When the stainless steel pyrolysis vessel was used, this organic layer had two distinctly different colored layers -- a light yellow and a dark brown. These organic layers did not stay separated when they mixed in the separatory funnel. Moreover, when the stainless steel pyrolysis apparatus was used but the rate of heating reduced, the organic product took another form. The product then formed one distinct yellow-brown mixture with the color yellow more apparent. This organic product was again different when the glass pyrolysis vessel was used. The product then usually was a more uniformly colored brown liquid with a green tint towards the

Table 3. Fuels from Aged and Fresh Soaps

<u>Soap</u>	<u>%Yield</u>	<u>Iodine Val.</u>	<u>Acid No.</u>	<u>Viscosity</u>	
				<u>Initial</u> <u>(cSt)</u>	<u>Final</u> <u>(cSt)</u>
fresh	16.7	149	1.0	65.8	109.1
				68.1	110.1
fresh	17.4	150	1.4	70.1	105.8
				69.9	107.4
aged	49.5	136	0.7	82.8	115.3
				80.1	108.8
aged	45.0	141	0.7	78.5	105.1
				77.5	107.4

end of recovery.

A possible explanation for the significant difference in yields between the glass and stainless steel pyrolysis vessels will now be discussed. As the soaps were heated, they vaporized in both vessels, and polymerization could take place in the vapor phase. This could happen more readily in the stainless steel pyrolysis apparatus for two reasons. First, there was a longer retention time with the stainless steel apparatus because of the extra volume provided by the glass top. Second, polymerization was possibly catalyzed by components in the stainless steel vessel. The polymers could then condense, and, since they would be much less volatile than the soaps, they would char rather than vaporize.

The thickening effects of the fuels obtained from the aged and fresh soaps were different. The kinematic viscosities for the fuels from the aged soaps increased an average of 36.9 percent while the average increase was 57.8 percent from the fresh soaps. However, it is interesting to note that the viscosities taken after 48 hours were very close for the fuels from both soaps: they averaged 112.0 and 106.3 centistokes when using aged soaps, compared to 109.6 and 106.6 centistokes when using fresh soaps. The average initial viscosities of the fuels from aged soaps (81.5 and 78.0 centistokes) were much greater than those of fuels from fresh soaps (67.0 and 70.0 centistokes). This shows that fuels from soaps aged the longer period of time had greater initial kinematic viscosities, but that the fuels from both types of soaps had approximately the same kinematic viscosities after 48 hours. Some of this variation in initial viscosity might have been due to the switch that occurred in the pyrolysis apparatus.

Glycerol Content of the Soaps

The second set of experiments for the pyrolysis studies investigated the effect of glycerol content of the soaps on the fuel (Table 4). The soap was again prepared by the fusion method using linoleic acid and 50 percent excess calcium hydroxide mixed with 71 grams of demineralized water. High speed lubrication oil was used for the polymerization tests. Fuels made from soaps without added glycerol were compared with fuels made from soaps having either 23 or 46 grams of glycerol added prior to pyrolysis. One mole of glycerol would be produced from vegetable oil for every three moles of calcium soap; 46 grams of glycerol corresponds to that amount. The 23 grams of glycerol was investigated to determine the effect if the glycerol was only partially removed prior to pyrolysis.

The glycerol content of the soaps did not change the properties of the fuel significantly. The acid numbers for the fuels from soaps without added glycerol were 1.0 and 1.3, while acid numbers ranged from 1.6 to 1.9 for fuels made from soaps with added glycerol. Iodine values showed this same consistency for the fuels that could be tested. Because the yields were only

Table 4. Fuels from Soaps With Different Amounts of Glycerol

Glycerol Added	%Yield	Iodine Val.	Acid No.	Viscosity	
				Initial (cSt)	Final (cSt)
none	12.6	134	1.3	81.8	100.3
none	13.7	124	1.0	72.7	107.0
23g	11.6	129	1.9	74.9	110.9
23g	10.7	131	1.9	75.7	109.8
46g	5.8	---	1.6	77.8	108.5
46g	4.5	---	1.7	76.9	107.1

5.8 percent and 4.5 percent for the fuels obtained with 46 grams of glycerol added, not enough product was available for an iodine value determination. Iodine values for the fuels from soaps without added glycerol were 134 and 124, while those from soaps with 23 grams of added glycerol were 129 and 131. The NMR spectra again confirmed the findings of small acid numbers and significant unsaturation.

Thickening effects of the fuels were not appreciably affected by the addition of glycerol to the soaps prior to pyrolysis. The kinematic viscosity for the fuels from soap with no added glycerol increased an average of 34.9 percent after 48 hours. Likewise, the kinematic viscosity for the fuels from soaps with 23 and 46 grams of added glycerol increased an average of 46.6 percent and 39.4 percent. This leads to the conclusion that glycerol content of the soaps does not affect the performance of the resulting fuels relative to their tendency to polymerize in a diesel engine.

However, the glycerol content of the soap did decrease the fuel yields per 100 grams of dry soap. Yields were low because pyrolysis was done in the stainless steel apparatus. Yields obtained from soaps with no glycerol added, with adding 23 grams, and with adding 46 grams averaged 13.2 percent, 11.2 percent, and 5.2 percent, respectively. The pattern of decreasing yield with increasing glycerol added to the soap leads to the conclusion that glycerol is not desirable in the soap prior to pyrolysis.

Fatty Acid Content of Soaps

The next task was an investigation of the effect of the fatty acid content of the soaps. The fusion method with linoleic acid was used to produce the soaps, and the polymerization tests used the high speed lubrication oil. A problem occurred when an attempt was made to increase the fatty acid concentration. The first approach was to heat the soap to form a liquid and then add the fatty acid (linoleic acid); then the corresponding acid number could be measured to determine the fatty acid content. The problem was that the soap would not melt before starting to pyrolyze. The next approach was to use excess linoleic acid during the preparation of the soaps. Several attempts were made but the technique proved to be a failure -- solid soap never formed, it just remained in the liquid state. Finally, it was decided to determine how much excess calcium hydroxide was required to produce a solid soap. After several runs it was discovered that solid soap required at least stoichiometric amounts of calcium hydroxide which would leave no free fatty acid if complete reaction could be attained. The two soaps compared in this task were prepared using 50 percent excess and stoichiometric amounts of calcium hydroxide. Although this was not the comparison that was to be made initially, it was the best that could be accomplished.

The results are given in Table 5. The properties of the fuels seemed to be somewhat dependent on the amount of excess

Table 5. Fuels from Soaps with Different Free Fatty Acid Contents

<u>Ca(OH)₂</u>	<u>%Yield</u>	<u>Iodine Val.</u>	<u>Acid No.</u>	<u>Viscosity</u>	
				<u>Initial (cSt)</u>	<u>Final (cSt)</u>
50%xs	43.8	132	0.6	76.7	106.3
				77.7	101.9
50%xs	54.5	139	0.6	75.9	105.1
				77.6	107.4
0%xs	41.2	181	6.1	76.5	117.8
				76.7	118.1
0%xs	43.9	184	8.1	76.9	120.0
				76.9	121.4

calcium hydroxide used. The acid numbers of fuels from soaps with a stoichiometric amount of calcium hydroxide were 6.1 and 8.1, while those from soaps with a 50 percent excess amount of calcium hydroxide were both only 0.6. Iodine values also differed: 181 and 184 for fuels from soaps with a stoichiometric amount of calcium hydroxide, and 132 and 139 for fuels from soaps with a 50 percent excess amount of calcium hydroxide. Therefore, fuels made from soaps with less calcium hydroxide had more unsaturation and more free fatty acid content. Yields were not significantly affected by the amount of calcium hydroxide used to prepare the soaps; they averaged 42.6 percent and 49.2 percent for the stoichiometric and the 50 percent excess calcium hydroxide, respectively. The glass pyrolysis apparatus was used for all these experiments.

The thickening of the fuel was affected by the free fatty acid content of the soaps. Kinematic viscosities increased an average of 54.5 percent and 36.7 percent for the fuels from soaps with the higher free fatty acid content and the lower free fatty acid content, respectively. These differences were due to the final kinematic viscosities of the fuels because the initial kinematic viscosities were all within 1.8 centistokes. It is obvious that fuels made from soaps with the higher free fatty acid content showed a tendency to polymerize faster. This probably would have been more significant if higher free fatty acid contents could have been achieved.

Calcium Versus Magnesium Soaps

The fourth study compared calcium soaps with magnesium soaps. The magnesium soap was prepared by the fusion method using linoleic acid and 33.1 grams of magnesium hydroxide mixed with 59 grams of demineralized water. The results from the tests in the pyrolysis studies were used for the calcium soap. Magnesium soaps gave such low yields that not enough product was available for any tests. Although the stainless steel pyrolysis apparatus was used, observable differences were still obtained. With this apparatus, typical yields from other runs in the pyrolysis studies using calcium soaps were about 10 to 15 percent, while yields using the magnesium soaps approached 0 percent. Thus, the calcium soaps were superior to the magnesium soaps since because of their higher yields.

A possible explanation of this yield difference may parallel the previous discussion of the difference in yields between the stainless steel and glass pyrolysis vessels (see "Aged Versus Fresh Soap" under the "Pyrolysis Studies" section). It is possible that the magnesium in the soaps promotes vapor phase polymerization more than does the calcium found in the soaps; this could result in decreased yields as previously discussed.

Also, the literature indicates magnesium soaps may have lower pyrolysis temperatures than their calcium counterparts. In the 1920s, Sato in Japan investigated the dry distillation of calcium and magnesium soaps of soybean oil and found that the

magnesium soaps decomposed at lower temperatures and gave heavier products than did the calcium soaps [11].

Distillation Results

The next pyrolysis study investigated the different fractions of the diesel fuel. Fuel and the fractions of the fuel corresponding to the #2 diesel range were used with high speed lubrication oil for polymerization tests. Soap was again prepared by the fusion method using linoleic acid and a 50 percent excess amount of calcium hydroxide mixed with 71 grams of demineralized water. The total distillate was made up of extremely light, #1, #2, #3, and extremely heavy liquid diesel products. The #2 fraction of the total distillate was 51 weight percent of the total product, and the fractions that were lighter and heavier than the #2 range fuel fraction were approximately equal. The total distillate was compared to the #2 range (Table 6). This comparison indicated the differences in the properties of the fuels were not significant. Acid numbers for the total distillate were 0.6 and 0.8 compared to acid numbers of 0.8 and 0.9 for the #2 diesel range. Iodine values for the total distillate were 136 and 130, while those for the #2 diesel range were 141 and 138.

However, thickening effects were somewhat different when the total distillate and the #2 diesel range product were compared. The total distillate had initial viscosities of 82.0 and 81.0 centistokes and final viscosities after 48 hours in the polymerization apparatus of 110.1 and 106.7 centistokes. The #2 diesel range had average initial viscosities of 62.2 and 63.6 centistokes and final viscosities after 48 hours in the polymerization apparatus of 108.4 and 106.5 centistokes. The total distillate experienced a 33.0 percent average increase in kinematic viscosity after 48 hours, while the #2 diesel range had a 70.6 percent average increase. This difference in viscosity increase is primarily due to the lower initial viscosity of the #2 diesel range compared to the total distillate -- the final viscosities were about the same in both cases.

The total distillate was next separated into three fractions: lighter than #2, #2, and heavier than #2 diesel. These three fractions were then compared as shown in Table 7. The viscosity increases were 91.1 percent for the lighter fraction, an average of 70.7 percent for the regular #2 diesel, and 27.2 percent for the heavy fraction. Again, the increases differed primarily because of the different initial viscosities. However, the heavy fraction did have a lower final viscosity than the other two fractions.

These results indicate that for hot weather regular #2 should be made up of diesel on the heavier side of the #2 diesel range. This is standard industrial practice as confirmed by Tom Davis, a chemical engineer at the Farmers Union Central Exchange in Laurel, Montana.

Table 6. The Total Distillate Versus the #2 Diesel Range

<u>Fuel</u>	<u>Iodine Val.</u>	<u>Acid No.</u>	<u>Viscosity</u>	
			<u>Initial</u> <u>(cSt)</u>	<u>Final</u> <u>(cSt)</u>
total	136	0.6	82.0	110.1
total	130	0.8	81.0	106.7
#2	141	0.8	62.3 62.2	108.4 108.3
#2	138	0.9	63.6 63.7	106.5 106.5

Table 7. Viscosity Results for Diesel Fuel Types

<u>Fuel</u>	<u>Viscosity</u>	
	<u>Initial</u> <u>(cSt)</u>	<u>Final</u> <u>(cSt)</u>
light	56.4	107.8
regular (#2)	62.3	108.4
	62.2	108.3
	63.6	106.5
	63.7	106.5
heavy	77.9	99.1

Storage Effects

Next, storage effects on the fuel were studied. Fuel fresh from pyrolysis was tested and compared to fuel pyrolyzed and let stand for 10 weeks. Polymerization tests used high speed lubrication oil, and the soaps were prepared by the fusion method with linoleic acid and a 50 percent excess amount of calcium hydroxide mixed with 71 grams of demineralized water. Data for these experiments are given in Table 8. Properties of the fuel were not affected by storage. Fuel fresh from pyrolysis had acid numbers of 5.1 and 1.3; the aged fuels' acid numbers were 4.2 and 0.6. Iodine values for fresh fuels were 160 and 147; those for the aged fuels were 143 and 150.

Thickening effects were also similar. For fuel fresh from pyrolysis the kinematic viscosity increased an average of 49.7 percent during the polymerization test, while for fuel that had been aged 10 weeks, the kinematic viscosity increased an average of 39.3 percent. In conclusion, the fuel aged for 10 week behaved similarly in the simulation of the diesel engine.

Results for Pure Linoleic Acid

Finally, the pure linoleic acid was compared to the other results in the "Pyrolysis Studies" section. The iodine value for the linoleic acid was 153, which was comparable to the iodine values found for the soap-pyrolysis fuels. The acid number of 155 for the linoleic acid was significantly higher than that of the acid numbers of the soap-pyrolysis fuels. The polymerization results with high speed lubrication oil showed an initial kinematic viscosity of 96.4 centistokes and, after 48 hours, one of 178.0 centistokes. This is an 85 percent increase in thickening of the linoleic acid, which is significantly more than that of the soap-pyrolysis fuels. In addition, both the initial and final viscosities of the linoleic acid are much greater than the soap-pyrolysis fuels. Therefore, soap-pyrolysis fuels would work better than pure linoleic acid in a diesel engine with regard to the tendency to polymerize.

Pyrolysis With and Without Calcium Hydroxide Reactant

The next task after the pyrolysis studies was to investigate pyrolysis with and without the use of calcium hydroxide as a reactant. Calcium hydroxide was added just prior to the heating of the soaps because a review of the literature indicated that pyrolysis with calcium hydroxide may produce hydrocarbons [12]. Hydrocarbons (RH) would be a product in the following reaction of calcium soap with calcium hydroxide:



A charge of 12.37 grams of calcium hydroxide was the stoichiometric amount required if the soap contained no water. The precipitation soap-making process was used to prepare the soaps in this group of experiments to insure that no excess

Table 8. Aged Versus Fresh Fuels

Fuel	Iodine Val.	Acid No.	Viscosity	
			Initial (cSt)	Final (cSt)
fresh	160	5.1	77.5	111.0
fresh	147	1.3	71.7	112.0
aged	143	0.6	71.0	108.3
aged	150	4.2	85.6	108.0

calcium hydroxide would be present in the soaps. The precipitation method used a stoichiometric amount of sodium hydroxide mixed with 86 grams of demineralized water and a 50 percent excess amount of calcium chloride mixed with 176 grams of demineralized water. The amount of calcium hydroxide required on a wet basis could not be calculated until after the pyrolysis was performed because the moisture content of the soaps was unknown. It was determined after pyrolysis that the amount of calcium hydroxide required on a dry basis for the runs was 7.16 and 6.36 grams. Therefore, 12.37 grams was a 72.8 percent and 94.5 percent excess for the two runs using the calcium hydroxide reactant.

The results are given in Tables 9 and 10. The acid numbers and iodine values of the fuels show no significant differences with or without the calcium hydroxide addition. Acid numbers for fuels made without the calcium hydroxide were 3.2 and 2.3, while they were 4.2 and 0.6 for fuels with the calcium hydroxide. The iodine values for all the fuels ranged from 138 to 148. NMR spectra supported the findings of small acid numbers and significant unsaturation.

Yield, however, was significantly decreased when the calcium hydroxide was added. Yields per 100 grams of dry soap were 79.7 percent and 73.1 percent when calcium hydroxide was not used prior to pyrolysis compared to yields of 58.8 percent and 61.4 percent when calcium hydroxide was used. Therefore, yield is adversely affected by the addition of calcium hydroxide prior to pyrolysis.

Polymerization tests were run with both medium and high speed lubrication oil. These results showed the kinematic viscosity increase after 48 hours in the polymerization apparatus was somewhat greater for the fuels made without the calcium hydroxide addition than for fuels with the addition. With the high speed lubricating oil (SAE 30W), the viscosity increase averaged 54.2 percent without the addition of calcium hydroxide and 41.8 percent with the addition. When the medium speed lubrication oil (SAE 40W) was used, the kinematic viscosity increase averaged 68.7 percent (ignoring run 3) without the addition and 61.8 percent with the addition of calcium hydroxide. Looking at the final viscosity readings for all eight runs, the value of 255.9 centistokes in run 3 of the medium speed oil was the only one out of line and was probably in error. These results indicate the addition of calcium hydroxide prior to pyrolysis is slightly beneficial in reducing thickening effects.

Control polymerization runs were also made using the lubricating oil without added soap-pyrolysis fuel (neat lubricating oil). The Table 10 data indicate the high speed lubricating oil was much more resistant to polymerization than the medium speed oil; the kinematic viscosity of the former increased 3.7 percent and the latter increased 32.0 percent in 48 hours. Therefore, because the differences in viscosity increase between the two lubricating oils were comparable whether or not soap-pyrolysis fuel was added, it appears that the addition of

Table 9. Experiments With/Without Calcium Hydroxide Reactant

<u>Run</u>	<u>Soap</u>	<u>%Yield</u>	<u>Iodine Val.</u>	<u>Acid No.</u>
1-w/o	1	79.7	148	3.2
2-with	1	58.8	138	4.2
3-w/o	2	73.1	145	2.3
4-with	2	61.4	140	0.6

Table 10. Viscosity Results of Fuels With/Without Reactant

<u>High Speed Lubricating Oil Viscosity</u>			<u>Medium Speed Lubricating Oil Viscosity</u>		
<u>Run</u>	<u>Initial (cSt)</u>	<u>Final (cSt)</u>	<u>Run</u>	<u>Initial (cSt)</u>	<u>Final (cSt)</u>
1	76.9	115.7	1	118.9	200.6
2	76.6	109.3	2	118.6	190.9
3	72.8	115.1	3	117.2	255.9
4	77.4	109.2	4	121.5	197.7
neat lub. oil	109.3 108.2	112.5 113.0	neat lub. oil	175.0 179.0	234.2 233.0

soap-pyrolysis fuels has about the same effect on both high speed and medium speed lubricating oils.

Soap Production

The next milestone investigated the effects of the soap production processes on fuel yields and the polymerization properties of the fuels. High speed lubricating oil was used for the polymerization tests. Until this milestone, soap had been produced using linoleic acid because (1) it was simpler and (2) the variables that were pertinent to the soap-pyrolysis process rather than the soap-production process had been the subject of investigation. Now it was time to use safflower oil because the fuel yields from the starting vegetable oil were important process information. The oil used for these experiments was mill run safflower oil from Elders Grain Company in Culbertson, Montana. The safflower oil was freshly extracted from a number of common varieties. The raw safflower oil was kept in refrigerated storage. Even though safflower oil is made up of primarily linoleic acid, the soap-making procedure was not expected to be exactly the same. This was because (1) the reaction of linoleic acid with calcium hydroxide produced calcium soap and water while (2) the reaction of safflower oil and calcium hydroxide produced calcium soap and glycerol. These experiments compared the fusion soap-making process with the precipitation method. Toluene and water at different concentrations were used as solvents with the calcium hydroxide in the fusion procedure as well as using no solvent at all.

The results of the pyrolysis studies were used as a guide for deciding the techniques to use. First, it was decided that no advantage was gained by drying the soaps. Second, glycerol was removed by pouring off any excess and then washing with demineralized water. Third, since the magnesium hydroxide dramatically decreased yield, calcium hydroxide was chosen as the alkali hydroxide.

The soap production method is outlined for both the precipitation and fusion methods in the "Experimental Description" section. Two batches of soap were prepared using the precipitation procedure and 180 grams of safflower oil; a solution of 25.7 grams of sodium hydroxide mixed with 77 grams of demineralized water was then added. Next a solution of 26.4 grams of calcium chloride and 79.2 grams of demineralized water was added. The sodium hydroxide was in a stoichiometric quantity, and the calcium chloride corresponded to a 50 percent excess.

The remaining batches of soap were prepared using the fusion method. Twenty-nine grams of calcium hydroxide were used for all the fusion runs; this corresponded to a 10 percent excess. First, two batches of soap were prepared with 200 grams of safflower oil and a slurry containing 29 grams of calcium hydroxide and 52 grams of demineralized water. Second, two more batches of soap were prepared with 200 grams of safflower oil and

a slurry with 29 grams of calcium hydroxide and 132 grams of demineralized water. Third, two batches of soap were prepared with 200 grams of safflower oil and only the 29 grams of calcium hydroxide. The most apparent difference when the safflower oil was used instead of the linoleic acid was the length of time required for the reaction to take place with the fusion process. With the safflower oil, agitation was required for 1.5 to 2.0 hours before the reaction was complete. When linoleic acid was used the reaction was complete in a matter of minutes. If this agitation was not sustained, the soap tended to want to separate out into two phases that looked like safflower oil and a calcium hydroxide solution.

Soap was then made by the fusion method, but with a hydrocarbon as the solvent instead of water. The reason for trying this was that a hydrocarbon such as toluene might provide better contact between phases. First, two batches of soap were prepared with 200 grams of safflower oil and a slurry of 29 grams of calcium hydroxide and 11 grams of toluene. Second, two batches of soap were prepared with 200 grams of safflower oil, 29 grams of calcium hydroxide, and 22 grams of toluene. Several different approaches had been initially tried for the set of runs that used toluene as the solvent. The 29 grams of calcium hydroxide were first tried with 50 grams of toluene. This produced very little soap with about 90 ml of unreacted safflower oil and glycerol. Next, 50 grams of toluene and 50 grams of calcium hydroxide were used to produce the soap. This produced more soap than the first method, but it still left approximately 35 ml of unreacted safflower oil and glycerol. The quantities of soap produced by these two methods were not large enough for subsequent pyrolysis. It was then determined that toluene in the concentrations finally used worked satisfactorily with the 29 grams of calcium hydroxide; very little unreacted safflower oil or glycerol remained, and there was enough soap for pyrolysis. The time required for this reaction to take place was about two hours.

The test results on the fuels are given in Table 11. As in previous tests, all the acid numbers and iodine values for the fuels produced by the various soap-making methods were quite similar. Acid numbers for the fuels ranged between 0.9 and 2.7. Iodine values were in the range of 151 to 170. No differences existed between the fuels in the amount of unsaturation or free fatty acid content. NMR spectra were all similar for the fuels produced from different soaps, and the spectra showed only a slight carboxylic acid peak and significant unsaturation. Again the NMR spectra confirmed the findings of the acid numbers and iodine values.

The thickening effects for the fuels obtained from soaps made by different procedures did not show significant deviations. The kinematic viscosity increase averaged 48.7 percent for the fuels from the precipitation soaps, 42.5 percent for both fusion soaps made with 52 and 132 grams of demineralized water, 47.4 percent and 46.6 percent for the fusion

Table 11. Results of Fuels from Different Soaps With and Without Solvent

<u>Soap Prep.</u>	<u>Iodine Val.</u>	<u>Acid No.</u>	<u>Viscosity</u>	
			<u>Initial</u> <u>(cSt)</u>	<u>Final</u> <u>(cSt)</u>
precipitation	158	1.5	77.3	120.2
precipitation	162	2.4	76.7	108.9
fusion 52g H ₂ O	151	1.9	78.9	109.8
fusion 52g H ₂ O	162	1.9	78.4	114.3
fusion 132g H ₂ O	166	2.3	82.2	117.7
fusion 132g H ₂ O	159	0.9	81.8	116.0
fusion 11g tol.	170	2.7	76.0	115.4
fusion 11g tol.	161	2.5	76.9	110.0
fusion 22g tol.	160	2.1	74.9	112.5
fusion 22g tol.	155	2.1	80.3	114.8
fusion (no solvent)	157	1.7	78.8	114.3
fusion (no solvent)	164	2.4	79.9	116.3

soaps made with 11 and 22 grams of toluene respectively, and 45.3 percent for the fusion soaps made with no solvent. Therefore, with respect to thickening effects in a diesel engine, the fuels made from different soap-making procedures would behave similarly in a time period of 48 hours.

Two types of yields were calculated as described in the "Experimental Description" section; these yields are given in Table 12. The first yield was calculated per 100 grams of dry soap. Table 12 data indicate that the precipitation and the fusion soap production method with no solvent gave the greatest fuel yields. The precipitation soap gave an average yield of 41.9 percent while the fusion soap produced with no solvent gave an average yield of 40.2 percent. Pyrolysis run 10 using soap with 22 grams of toluene solvent had the greatest yield of 66.1 percent, but this was not confirmed by its duplicate run 9 with a yield of 34.3 percent.

A second yield was calculated per 100 grams of total safflower oil used. Some of the duplicate data for this calculation were inadvertently destroyed, but at least one value for each of the soaps was saved. These values along with the first set of yields provided enough information for a pattern to be recognized and a recommendation to be made. Again, the soaps using the precipitation method and the fusion method without any solvent gave the highest fuel yields. The yields on Table 12 show the precipitation soap process had a 45.9 percent yield, and the fusion soap method with no solvent gave yields of 43.6 percent and 39.1 percent. As previously mentioned in the "Experimental Section" under "Soap Production," more steps, and ultimately more time, are required for soap preparation with the precipitation method than with the simpler fusion process. Even when the fusion method is complicated slightly by the use of safflower oil rather than linoleic acid, it is still easier to perform than the precipitation method.

A soap-making procedure can therefore be recommended. First, the fuels made with these different soaps demonstrated that only a negligible difference would exist in a diesel engine with regard to tendency to polymerize within 48 hours. Second, the precipitation soap-making process and the fusion method with no solvent gave the greatest yields -- these were about the same. Because the fusion method with no solvent is a one-step process and the precipitation method is a multi-step one that is harder to perform and takes more time, the fusion process is preferred. Also, using a solvent of any kind is not recommended because they decrease the yield.

Unsaturation Studies

The mechanism by which polymerization proceeds has been described by Rheineck and Austin [13] as follows:

1. An induction period occurs, preceding the initiation of the oxidative chain reaction, during which no visible physical or chemical properties change.

Table 12. Yields of Fuels from Different Soaps With and Without Solvent

<u>Soap Prep.</u>	<u>Yield (g fuel/ 100g dry soap)</u>	<u>Yield (g fuel/ 100g safflower oil)</u>
precipitation	44.8	45.9
precipitation	38.9	
fusion 52g H ₂ O	24.2	23.4
fusion 52g H ₂ O	26.2	
fusion 132g H ₂ O	26.9	16.6
fusion 132g H ₂ O	26.4	
fusion 11g tol.	26.3	30.0
fusion 11g tol.	29.2	
fusion 22g tol.	34.3	33.8
fusion 22g tol.	66.1	
fusion (no solvent)	42.6	43.6
fusion (no solvent)	37.7	39.1

2. Oxygen interacts with carbon double bonds to form hydroperoxides. A considerable uptake of oxygen coincides with the beginning of a perceptible polymerization reaction.
3. The polyunsaturated species undergo conjugation of double bonds and isomerization of cis to trans forms.
4. The hydroperoxides decompose resulting in free radicals which in turn contribute to autocatalysis.
5. Production of high-molecular weight cross-linked polymers and low-molecular weight carbonyl and hydroxyl compounds occurs via free radical polymerization and scission reactions.

The number of fatty acid double bonds should then affect reactivity. In addition, Miyashita and Takagi [9] recently proposed that higher oxidative rates of free fatty acids than those of their methyl esters could be due to the catalytic effect of the carboxyl groups on the formation of free radicals by the decomposition of hydroperoxides. It is a possibility then that number and/or position of the carboxyl groups relative to the carbon double bonds would affect the polymerization reaction.

Previous research in this lab [8] indicated that the polymerization properties of the fuel produced by a soap-pyrolysis process may not be very sensitive to the quantity of unsaturation. It was found that the polymerization character was more sensitive to the free fatty acid content. The purpose of the unsaturation studies was to investigate the effect of unsaturation on polymerization with high speed lubrication oil. This was done by preparing soaps that were made from fatty acids with varying degrees of unsaturation. The fatty acids all had 18 carbon atoms with different numbers of carbon double bonds: stearic acid (saturated), oleic acid (one double bond), linoleic acid (two double bonds), and linolenic acid (three double bonds). The effect of unsaturation can be determined more specifically using the technical grade fatty acids than using a safflower oil composed of a mixture of esters made from acids with different degrees of unsaturation and different numbers of carbon atoms. Soap was prepared by the fusion method using each of the four fatty acids. An interesting observation was that the soaps from each fatty acid had a distinctive color: off-white for the stearic acid soap, light gray for the oleic acid soap, light tan for the linoleic acid soap, and medium tan for the linolenic acid soap. Pyrolysis of all the soaps except that of stearic acid produced fuels suitable for further testing. Because stearic acid is a solid at room temperature, the fuel produced from it also had a high melting temperature compared to those fuels from other fatty acids. When pyrolysis was run on the soap produced from stearic acid, the resulting fuel solidified when cooled in the condenser leading to the product collection vessel and plugged the apparatus. Because a solid fuel is not at all attractive for use in a diesel engine, it was decided to eliminate the stearic acid soap from further tests.

The results are presented in Table 13. The acid numbers of the fuels are all relatively low and indicate little free fatty acid content. The average acid numbers were 0.2 for the oleic

Table 13. Results of Fuels From Different Acid Soaps

<u>Fuel</u>	<u>%Yield</u>	<u>Iodine Val.</u>	<u>Acid No.</u>	<u>Viscosity</u>	
				<u>Initial</u> <u>(cSt)</u>	<u>Final</u> <u>(cSt)</u>
oleic acid soap	69.2	132	0.2	79.0 77.6	97.7 99.0
	65.4	141	0.2	76.2 75.2	95.9 99.6
linoleic acid soap	59.4	147	0.6	79.2 78.6	109.3 109.9
	62.7	148	0.6	78.7 77.3	106.7 107.7
linolenic acid soap	59.1	143	0.6	79.1 78.2	104.8 103.1
	57.4	150	0.4	78.5 78.8	107.0 106.3

oleic acid soaps, 0.6 for the linoleic acid soaps, and 0.5 for the linolenic acid soaps. Because the starting acids were all monocarboxylic, i.e., they contain only one carboxylic or acid group, the acid numbers were all similar: 157 for oleic, 155 for linoleic, and 162 for linolenic. The iodine values of the fuels were all similar, while those of the starting acids increased with increasing unsaturation. The values of the starting acids are understandable (106 for oleic, 153 for linoleic, and 190 for linolenic), because iodine value is a measure of the number of carbon double bonds present and oleic has one double bond, linoleic has two double bonds, and linolenic has three double bonds. However, the similarity of the iodine values of the fuels made from soaps produced from these acids is surprising. The literature has indicated that double bonds can be formed during soap-pyrolysis, particularly if calcium hydroxide is present. This would explain the increase in unsaturation in the fuel using the oleic acid soap [12]. It was also found that soaps are often used as driers to promote oxidation and polymerization of unsaturated vegetable oils. This would lead to a decrease in unsaturation as some double bonds are eliminated in forming larger molecules. The carbon 13 NMR spectra confirmed the findings of essentially no carboxylic acid groups present and a significant amount of unsaturation.

The yield data calculated per 100 grams of dry soap indicate yield decreased as unsaturation in the original acid has increased. The average yields of fuels were 67.3 percent from the oleic acid soap, 61.1 percent from the linoleic acid soap, and 58.3 percent from the linolenic acid soap. In 1939 Dalal and Mehta in India cracked vegetable oils. They found that liquid product yields decreased with increasing unsaturation [14]. This pattern of decreasing yield with increasing unsaturation in vegetable oils has therefore been documented before.

Polymerization tests were performed with the high speed lubrication oil. The values from the table indicate that initial kinematic viscosities for each of the fuels from different soaps were similar. These viscosities averaged 77.0, 78.5 and 78.7 centistokes for the fuel from the oleic, linoleic, and linolenic acid soaps, respectively. After 48 hours in the polymerization apparatus, the kinematic viscosities of all the fuels had increased. The increase for the fuels averaged 27.4 percent for fuel from the oleic acid soap, 38.2 percent for the fuel from the linoleic acid soap, and 34.0 percent for the fuel from the linolenic acid soap. It is interesting to note that the values of the viscosities taken after 48 hours and the iodine values of the starting fuels are almost directly proportional. For both properties the values increased in order of oleic, linoleic, and linolenic (values for the linoleic and linolenic fuels were very close, however).

The purpose of this task was to investigate the effect of unsaturation on polymerization. Results from previous research [8] had suggested that the effect of unsaturation on polymerization might be less important than the free fatty acid

content present. The unsaturation studies conducted here cannot distinguish between these two variables, because all the starting soap-pyrolysis fuels had little free fatty content as evidenced by the acid numbers and qualitatively confirmed by the NMR spectra.

Several conclusions can be drawn from this study. First, soap made from stearic acid is undesirable, because the fuel was a solid at ambient conditions. Second, it might be desirable for the vegetable oil to contain more oleic acid esters than either linoleic or linolenic acid esters. The fuel yields would probably be greater, and there may be less tendency to polymerize with the lubrication oil. Finally, when virtually no free fatty acids are present, iodine values serve as a good indication of polymerization characteristics.

Soap-Pyrolysis Process Optimization

This task optimized the soap-pyrolysis process for making fuel suitable for use in a diesel engine. The results from the previous experiments helped identify important process variables and techniques that were used in this task. The purpose of the optimization study was to put all the prior results together and determine the combination of the most desirable techniques and levels of variables for the process.

Several variables that affected the fuel were observed from the previous experiments and optimized here. First, the "Pyrolysis Studies" tests addressing the "Fatty Acid Content of the Soap" indicated that the amount of calcium hydroxide added to the linoleic acid during soap production might affect polymerization characteristics. This optimization used safflower oil instead of linoleic acid to produce the soaps because it was important to compare fuel yields from the vegetable oil. Therefore, the first variable optimized was the amount of excess calcium hydroxide added to the safflower oil to make the soaps. The lower constraint on the amount of calcium hydroxide added to 200 grams of safflower oil was 0 grams of excess (stoichiometric) or 26.3 grams. Second, it was shown that, when pyrolysis was performed with the addition of calcium hydroxide reactant, the addition of calcium hydroxide to the linoleic acid prior to pyrolysis decreased thickening while limiting yield. This was the second variable optimized. The lower constraint on this variable was to add no (0 grams) calcium hydroxide prior to pyrolysis.

Several techniques were also found to affect the fuel. First, the "Pyrolysis Studies" reported under the "Glycerol Content of the Soaps" section found that glycerol in the soap decreased yield. Therefore, the glycerol was removed by washing the soaps with demineralized water and pouring off any on the surface of the soap. Second, the studies discussed under "Soap Production" indicate that the soap should be prepared by the fusion method with no solvent. This procedure was used to prepare all the soaps for this task.

Optimization of the process included several steps. The yield of the fuel was selected for optimization. The polymerization characteristics were considered to be less important because all the soap-pyrolysis fuels were satisfactory and quite consistent in this respect. First, the Sequential Simplex optimization procedure was used as long as possible [15]. The number of variables to be optimized was two, so the number of vertices in a simplex was three. The simplex vertices corresponded to the various levels of the variables. After comparing the three experiments, a decision was made to discard the worst experiment. The location of the new experiment was calculated by using simple rules, and this resulted in a new simplex. This technique was abandoned when it was found that the constraints were starting to be violated, i.e., it would require using less than the amount of calcium hydroxide required to produce the soaps or a negative (impossible) amount of calcium hydroxide added prior to pyrolysis. This made it futile to maintain the original shape of the simplex (See Figure 6).

The Complex Method of Box [15] was next implemented to locate the optimum. The Complex Method of Box is superior to the simplex method in that the shape of the pattern of experimental runs can be changed; this allows for continued experimentation without violating any variable constraint. This technique used four vertices which again corresponded to the levels of variables (See Figure 7). The location of the next experiment was found again by discarding the least desirable point and using simple rules to find the new point in the complex. From this method the optimum appeared to be at values of 0 excess grams of calcium hydroxide for soap production and 0 grams of calcium hydroxide added prior to pyrolysis. The results of this procedure are given in Table 14 and indicate that the yields at or very near this point were the greatest, while the kinematic viscosities of all the experiments were good. Runs 3 and 7 are duplicates of each other. Run 7 was performed because the run 3 yield looked suspicious. The run 7 yield of 24.8 percent showed that the Run 3 yield of 36.8 percent was out of line and probably in error.

Once the optimum appeared to be found, a factorial experimental design was used to fit an equation to the surface of the yield as a function of the two variables [16]. The reason for obtaining this equation was to represent all possible yields over the ranges of the two variables rather than just the yields for the particular experimental runs that had been performed. An optimization technique could then be used to find the maximum yield on the surface; this would then be verified with an experimental run at optimum conditions. This factorial required nine experimental runs: three of the previous runs were used and six new experiments were made (Figure 8). The order of the new experiments was determined randomly. Table 15 shows the experiments for the 3^2 factorial and the corresponding yields and kinematic viscosities at each level.

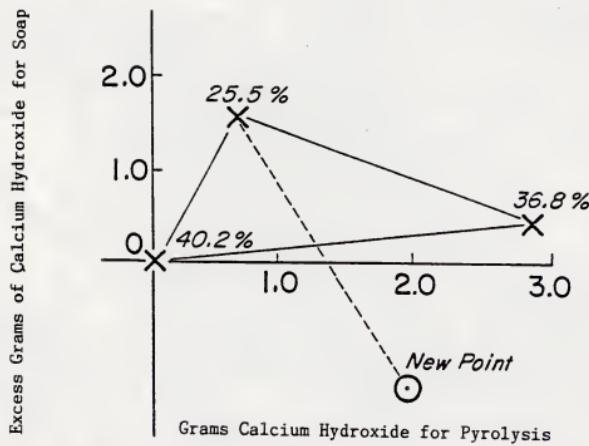


Figure 6. Variable Levels for Sequential Simplex Optimization Technique

Excess Grams of Calcium Hydroxide for Soap

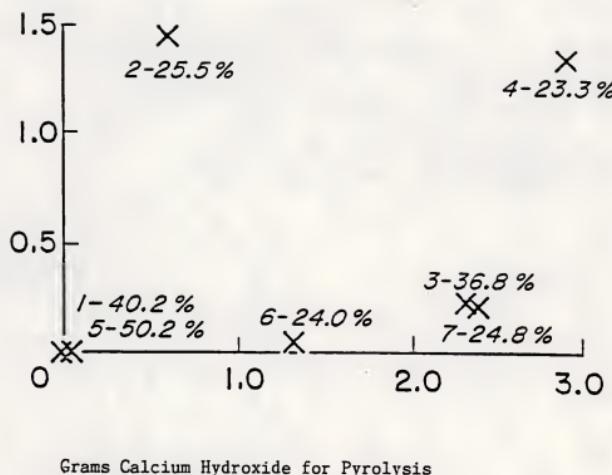


Figure 7. Variable Levels for Complex Method of Box Optimization Technique

Table 14. Results for the Complex Method of Box

Run	x_1 (g)	x_2 (g)	%Yield	Viscosity (HS) (cSt)		Viscosity (MS) (cSt)	
				Initial	Final	Initial	Final
1	0.0	0.00	40.2	79.2	125.6	138.9	189.8
2	1.45	0.78	25.5	82.3	131.7	133.6	198.8
3	0.39	2.90	36.8	81.7	110.5	143.9	212.5
4	1.50	3.00	23.3	76.9	109.1	119.3	200.6
5	0.03	0.00	50.2	79.8	115.3	126.3	207.5
6	0.03	1.26	24.0	80.1	122.7	136.2	202.2
7	0.39	2.90	24.8	77.3	112.1	136.8	184.8

Yield is calculated per 100 grams of safflower oil.

x_1 Excess of $\text{Ca}(\text{OH})_2$ used to make the soap

x_2 $\text{Ca}(\text{OH})_2$ added prior to pyrolysis

HS High speed lubrication oil

MS Medium speed lubrication oil

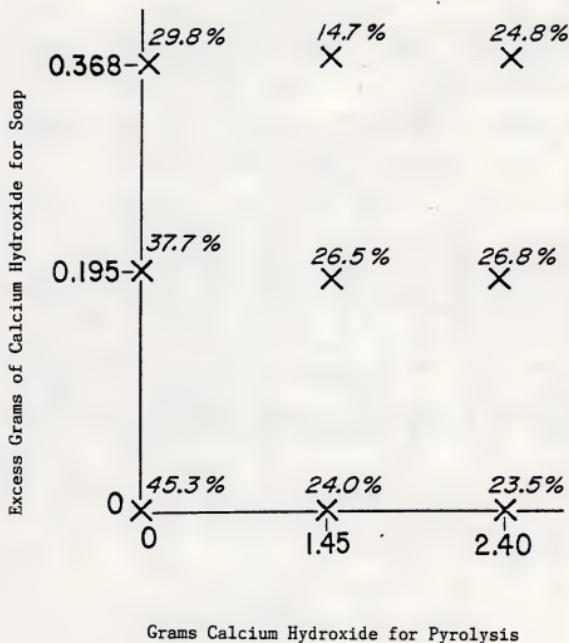


Figure 8. Variable Levels for the Factorial Experimental Design

Table 15. Results from the 3² Factorial

X ₁	X ₂	%Yield	Viscosity (HS) (cSt)		Viscosity (MS) (cSt)	
			Initial	Final	Initial	Final
0.015*\$	0.00	45.2*@	79.5*@	120.5*@	132.6*@	198.7*@
0.000	1.45	24.0@	80.1@	122.7@	138.2@	202.2@
0.000	2.90	23.5	78.1	114.2	126.5	190.2
0.195	0.00	37.7	77.8	114.2	132.7	188.6
0.195	1.45	26.5	79.0	108.6	133.1	188.8
0.195	2.90	26.8	79.2	115.8	130.0	185.0
0.368	0.00	29.8	82.0	116.2	129.0	184.3
0.368	1.45	14.7	73.2	119.3	108.0	199.4
0.390&	2.90	24.8@	77.3@	112.1@	136.8@	184.8@

* Averages of duplicate runs

§ Although this number should have been 0.0, it was close enough and could be used in the factorial experimental design

@ Taken from previous work in this study

& Although this number should have been 0.368, it was close enough and could be used in the factorial experimental design

The mathematical equation that describes the yield surface was:

$$y = B_0x_0 + B_1x_1 + B_2x_2 + B_{11}x_1^2 + B_{22}x_2^2 + B_{12}x_1x_2$$

where:

y = yield per 100 grams of safflower oil

x_1 = excess grams of $\text{Ca}(\text{OH})_2$ in soap

x_2 = grams of $\text{Ca}(\text{OH})_2$ added prior to pyrolysis

$B_0, B_1, B_2, B_{11}, B_{22}, B_{12}$ = constants

The procedure used to find the constants is described by Davies [16]. The levels of the variables are given in Table 16.

The equation was calculated to be:

$$y = 44.6 - 7.8x_1 - 20.4x_2 - 98.2x_1^2 + 4.6x_2^2 + 15.7x_1x_2$$

All the constants were determined to be significant.

There are many optimization techniques that can be used with an equation such as this one that represents the surface of all possible fuel yields. The objective is to use the equation to calculate the maximum fuel yield. The Complex Method of Box is reliable, and a computer program was written to use this technique. The values for x_1 and x_2 again correspond to the amount of excess calcium hydroxide used to make the soap and the amount of calcium hydroxide added prior to pyrolysis. The maximum fuel yield determined by the program was 44.6 percent and occurred at values of $0.315735577\text{E-}6$ for x_1 and $0.151638811\text{E-}6$ for x_2 . Therefore, the maximum yield can be said to occur essentially at the point $x_1=0$ and $x_2=0$.

One last run was done at the optimum using a stoichiometric amount of calcium hydroxide for soap production (0 grams excess) and no calcium hydroxide (0 grams) added to the soap prior to pyrolysis. In addition, duplicate polymerization tests were done along with an acid number and iodine value for this fuel. Table 17 gives the results for this final run. The data on this table do indeed indicate this was the point for maximum yield. This yield of 39.8 percent can be compared to a value of 44.6 percent predicted by the equation. This shows there is experimental variability present. The variability is further evidenced by runs 1 and 5 in Table 14. Performed at almost identical conditions, the yields were 40.2 percent and 50.2 percent.

The thickening characteristics are all similar to previous results in the optimization study. The kinematic viscosities for the fuels in the final run increased by different percentages with the high speed and medium speed lubrication oil. The viscosity of fuel used with the high speed lubrication oil increased an average of 47.9 percent, while the viscosity of fuel used with the medium speed lubrication oil increased an average of 73.7 percent. The failure point mentioned earlier in this report was a 375 percent increase in kinematic viscosity in 64 hours. Also, the acid number of 1.7 shows there is little free fatty acid content, and an iodine value of 158 displays significant unsaturation.

Several things were learned from the optimization studies. First, yield was effective for evaluating the differences between the fuels since changes in thickening properties were not as

Table 16. Variable Levels Used for Optimization

<u>Variable</u>	<u>Level (grams)</u>
x_1	0.000
	0.195
	0.368
x_2	0.000
	1.450
	2.900

Table 17. Final Run Results

	<u>Viscosities (HS)</u> (cSt)	<u>Viscosities (MS)</u> (cSt)					
<u>%Yield</u>	<u>Iodine Val.</u>	<u>Acid No.</u>	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>	
39.8	159	1.7	76.9 77.3	113.3 114.7	120.0 120.6	210.7 207.2	

significant. Second, the optimum values for the variables tested occurred with (1) a stoichiometric amount of calcium hydroxide added to the safflower oil for soap production and with (2) no calcium hydroxide reactant added to the soap prior to pyrolysis. The kinematic viscosity increased less after 48 hours in the polymerization apparatus when the high speed lubrication oil was used compared to using the medium speed lubrication oil. However, in reference to the results reported in the "Pyrolysis With and Without Calcium Hydroxide Reactant" section, the high speed lubrication oil is more resistant to polymerization than the medium speed lubrication oil. The control polymerization tests that were run with lubrication oil without any added soap-pyrolysis fuel showed that, after 48 hours in the polymerization apparatus, the high speed lubrication oil experienced a 3.7 percent increase in kinematic viscosity, while the medium speed had a 32.0 percent increase. Therefore, the differences in viscosity increases were probably due to the characteristics of the two lubricating oils rather than due to the addition of soap-pyrolysis fuels.

A final comparison is made between safflower oil and the soap-pyrolysis fuel. In previous work done in this lab for the soap-pyrolysis technique, straight safflower oil was tested [8]. The previous lubricating oil used for the polymerization tests was Phillips 66 HD II SAE 30W (similar to the present high speed lubrication oil), and a five weight percent concentration of safflower oil was used. The safflower oil experienced a 110 percent increase in kinematic viscosity in the polymerization apparatus from about 95 to 200 centistokes. In addition, the iodine value for the safflower oil was 149, and a typical acid number was 170. These results compared to the soap-pyrolysis fuels in this study indicate safflower oil has a greater tendency to polymerize than the soap-pyrolysis fuels when subjected to conditions of a simulation of a diesel engine. The most apparent chemical difference between safflower oil and soap-pyrolysis fuels is that the safflower oil has a much greater acid number. Iodine values of both the safflower oil and soap-pyrolysis fuels showed significant unsaturation.

OPTIMIZED PROCESS DESCRIPTION
AND PROCESS FLOWSHEET

A block flowsheet of the soap-pyrolysis process for converting safflower oil into diesel fuel is shown in Figure 9. the calculations that determined the quantities shown on the flowsheet can be found in Appendix 1.

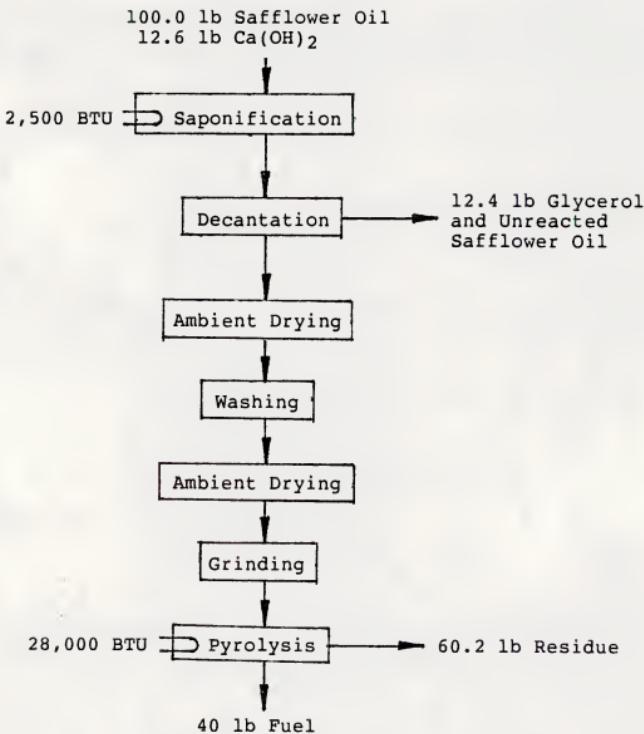


Figure 9. Block Flowsheet for the Soap-Pyrolysis Process for Converting Safflower Oil to Diesel Fuel

CONCLUSIONS AND RECOMMENDATIONS

The two properties that were observably affected by the soap-pyrolysis process variables were (1) the yield of fuel from the safflower oil and (2) the initial viscosity of the fuel-lubrication oil mixture. The polymerization tests indicated that after 48 hours the viscosities of the fuel-lubrication oil mixtures were less than or comparable to those of the lubrication oil alone regardless of the initial viscosities of the mixtures. Therefore, fuel yield is the only significant effect of the process variables.

Conclusions relative to fuel yield are:

1. The presence of glycerol in the soap prior to pyrolysis decreases yield. Therefore, wash the soap to remove glycerol.
2. Calcium soaps give higher yields than magnesium soaps. Therefore, use calcium soaps.
3. The addition of calcium hydroxide to the soaps prior to pyrolysis to promote the formation of hydrocarbons rather than aldehydes and ketones decreases the yield. Therefore, do not add calcium hydroxide to the soap prior to pyrolysis.
4. Whenever a solvent was used in the fusion soap-making process, the yield decreased. Therefore, do not use a solvent in the fusion soap-making process.
5. The fusion soap-making process without a solvent and the precipitation soap-making process give comparable yields, but the former process is much simpler. Therefore, use the fusion soap-making process.
6. Oleic acid soaps give higher yields than linoleic or linolenic acid soaps. Therefore, it would be desirable to increase the oleic acid ester content and decrease the linoleic acid ester content of safflower oil.
7. Excess calcium hydroxide added in the fusion soap-making process without a solvent significantly decreases the yield. Therefore, use the stoichiometric quantity of calcium hydroxide to make the soap.

The only quantitative process variable listed in the above conclusions is the amount of calcium hydroxide used in the fusion soap-making process without a solvent. This variable is quite sensitive, as the fuel yield was 45.2 weight percent with no excess, 37.7 weight percent with 0.74 percent excess calcium hydroxide, and 29.8 weight percent with 1.4 percent excess calcium hydroxide.

Relative to the application of the knowledge gained in this project, it now appears appropriate to progress from laboratory simulations of engine crankcase conditions to actual engine tests. This would involve the construction of a small pilot plant process to produce enough fuel for engine testing. To reduce costs it would probably be prudent to use a batch rather than continuous process. Engine tests would be used to verify the results of this project in an actual operating environment incorporating elements that cannot be readily duplicated in the laboratory, e.g., the question of whether the soap-pyrolysis fuel

is evaporating from the fuel-lubrication oil mixture would automatically be addressed. An extension to the present study would be to investigate the percentage of soap-pyrolysis fuel that could be added to the diesel fuel.

TECHNOLOGY TRANSFER ACTIVITIES

During the course of this project efforts were made to interact with others interested in the use of vegetable oils as a diesel fuel. Copies of milestone reports were sent to Mr. Chris Carroll at the Energy Extension Service in Presque Isle, Maine. Information about the project was also sent to D. I. Bransbury of Auburn University for a literature review relative to the conversion of biomass into fuels. Some polymerization tests were made for Dr. R. A. Korus of the University of Idaho on a mixture of methyl esters of rapeseed oil and high-speed lubrication oil -- that university does not have polymerization test apparatus. A paper will be prepared summarizing this project for submission to a reputable technical journal, e.g., The Journal of the American Oil Chemists Society.

APPENDICES

Appendix 1. Sample Calculations

Mass and Energy Balance Calculations for the
Soap-Pyrolysis Process

Basis: 100 lb Safflower Oil (SO)

Material Balance Calculations

1. $\text{Ca}(\text{OH})_2$ Feed

$$100 \text{ lb SO} \times \frac{\text{mol SO}}{878.9 \text{ g SO}} \times \frac{1.5 \text{ mol } \text{Ca}(\text{OH})_2}{1 \text{ mol SO}} \times \frac{74.1 \text{ g } \text{Ca}(\text{OH})_2}{\text{mol } \text{Ca}(\text{OH})_2}$$
$$= 12.6 \text{ g } \text{Ca}(\text{OH})_2$$

2. Glycerol Production

$$100 \text{ g SO} \times \frac{\text{mol SO}}{878.9 \text{ g SO}} \times \frac{1 \text{ mol glycerol}}{1 \text{ mol SO}} \times \frac{92 \text{ g glycerol}}{\text{mol glycerol}}$$
$$= 10.5 \text{ g glycerol}$$

3. Soap Production

$$100 \text{ g SO} \times \frac{\text{mol SO}}{878.9 \text{ g SO}} \times \frac{1.5 \text{ mol soap}}{1 \text{ mol SO}} \times \frac{598.6 \text{ g soap}}{\text{mol soap}}$$
$$= 102.2 \text{ g soap}$$

4. Glycerol and Unreacted Safflower Oil

11 wt% of saponification feed (experimental value)

$$(100 + 12.6) \text{ g saponification feed} \times 0.11 = 12.4 \text{ g glycerol}$$

and unreacted SO

5. Fuel Production

0.4 g fuel/ 1 g of safflower oil in feed (experimental
value)

$$100 \text{ g safflower oil} \times 0.40 = 40 \text{ g fuel}$$

Energy Balance Calculations

1. Saponification

ΔH° for saponification reaction = -30 kcal/mol SO at 25° C
(estimated from energy requirements that could be
calculated for alcohol hydration and saponification
reactions)

C_p for glycerol = 0.62 cal/(g-°C)
 C_p for soap = 0.55 cal/(g-°C)

Assume the feed enters at 25° C and the products leave at 100° C

$$\begin{aligned} Q &= 100 \text{ g SO} \times \frac{\text{mol SO}}{878.9 \text{ g SO}} \times \frac{-30 \text{ kcal}}{\text{mol SO}} \\ &\quad + 10.5 \text{ g glycerol} \times \frac{0.62 \text{ cal}}{\text{g-}^{\circ}\text{C}} \times (100 - 25)^{\circ}\text{C} \times \frac{1 \text{ kcal}}{1000 \text{ cal}} \\ &\quad + 102.2 \text{ g soap} \times \frac{0.55 \text{ cal}}{\text{g-}^{\circ}\text{C}} \times (100 - 25)^{\circ}\text{C} \times \frac{1 \text{ kcal}}{1000 \text{ cal}} \\ &= 1.287 \text{ kcal} \end{aligned}$$

$$\begin{aligned} Q &= 1.287 \text{ kcal} \times \frac{454 \text{ g}}{1 \text{ lb}} \times \frac{\text{BTU}}{0.252 \text{ kcal}} \\ &= 2319 \text{ BTU} \approx 2500 \text{ BTU} \end{aligned}$$

2. Pyrolysis

ΔH° for pyrolysis = 700 BTU/lb fuel at 25° C
(estimated from the heat of decomposition of petroleum feedstocks into gasoline)

$$\begin{aligned} Q &= 100 \text{ lb SO} \times \frac{0.40 \text{ lb fuel}}{1 \text{ lb SO}} \times \frac{700 \text{ BTU}}{1 \text{ lb fuel}} \\ &= 28,000 \text{ BTU} \end{aligned}$$

Appendix 2. References Cited

REFERENCES CITED

1. Rosenbaum, Walter A., Environmental Politics and Policy, Congressional Quarterly, Inc., Washington D.C., 1985, p. 220.
2. Duke, J. A., and M. O. Bagby, "Comparison of Oilseed Yields: A Preliminary Review," in Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, Fargo, North Dakota, 1982, pp. 11-23.
3. Quick, G. R., "An In-Depth Look at Farm Fuel Alternatives," Power Farming Magazine, 59(2), 1980, pp. 10-17.
4. Collins, G. S., R. C. Griffin, and R. D. Lacewell, "National Economic Implications of Substituting Plant Oils for Diesel Fuel," in Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, Fargo, North Dakota, 1982, pp. 138-148.
5. Simon, Julian L., "The Scarcity of Raw Materials," The Atlantic Monthly, 247(6), 1981, pp. 33-41.
6. Van der Walt, A. N., and F. J. C. Hugo, "Diesel Engine Tests with Sunflower Oil as an Alternative Fuel," in Proceedings of the Third International Conference of Energy Use Management, West Berlin, Permagon Press, 1981, pp. 1927-1933.
7. Windholtz, M., et al., The Merck Index, 10th ed., Merck and Co., Inc., Rahway, N.J., pp. 1197, 1293, 1234, 1903.
8. Hiebert, Dwight Randall, "Decarboxylation and Hydrogenation of Safflower and Rapeseed Oils to Produce Diesel Fuels", Master's Thesis, Montana State University, Bozeman, Montana, May 1985. Much of this information is also included in Scarrah, W. P., "Chemical Processing of Vegetable Oil Fuels to Prevent Polymerization," final report prepared for the Montana Department of Natural Resources and Conservation, Grant Agreement RAE-84-1041, July 1986.
9. Miyashita, Kazuo, and Toru Takagi, "Study on the Oxidative Rate and the Prooxidant Activity of Free Fatty Acids," J. Am. Oil Chem. Soc., 63(10), 1986, pp. 1380-1384.
10. CRC Handbook of Lubrication, Vol. 1, The American Rubber Company, Cleveland, Ohio, 1983.
11. Sato, M. J., "Preparation of Fuel Oil by the Dry Distillation of the Calcium Soap of Soya Bean Oil. IV. The Influence of Temperature on Distillation," J. Soc. Chem. Ind. (Japan), 30, 1922, pp. 242-245.
12. Markley, K. S., Fatty Acids: Their Chemistry, Properties, Production, and Uses, 2nd ed., Part 2, Interscience, New York, 1961.
13. Rheineck, A. E., and R. O. Austin, "Treatise on Coatings," edited by R. R. Myers and J. S. Long, Vol. 1, Part 2, Ch. 4, Marcel Dekker, New York, 1968.
14. Dalal, N. M., and T. N. Mehta, "Cracking of Vegetable Oils," J. Indian Chem. Soc. Ind. News Ed., 2, 1939 pp. 213-245.
15. Beveridge, Gordon S. G., and Robert S. Schechter, Optimization Theory and Practice, McGraw-Hill, New York, 1970.
16. Davies, Owen L., Design Analysis of Industrial Experiments, Hafner Publishing Co., New York, 1967.



